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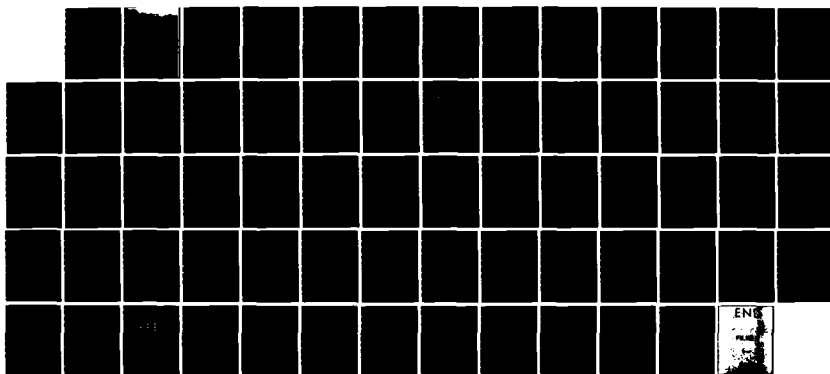
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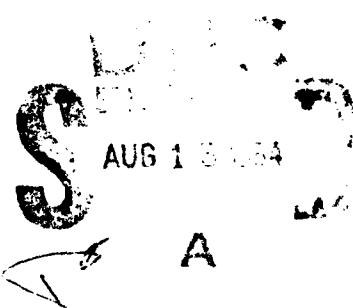
by

M. BALKANSKI and J. HAMMERBERG

Contract Number : DAJA 45-83-C-0025

Final Report

January-December 1985



The work reported in this document has been in part supported and sponsored by the Office of Naval Research, through the European Research Office, Durham, North Carolina, and the Office of Naval Research, Arlington, Virginia, and the Office of Naval Research, Durham, North Carolina.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
AD-A144252		
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
Solid State Batteries, Literature Survey, Analysis of Pertinent Results and Prospective for further research.		Final Technical Report JAN - DEC 1983
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER
M. Balkanski and J. Hammerberg		
9. PERFORMING ORGANIZATION NAME AND ADDRESS		8. CONTRACT OR GRANT NUMBER(s)
Laboratoire de Physique des Solides Universite Pierre et Marie Curie 4 Place Jussieu, Tour 13, 75230 Paris Cedex 05		DAJA45-83-C-0025
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS		
61102A IT161102EN5767		
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
USARLSC-UK Box 65 FPO NY 09510		JAN - DEC 1983
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office)		13. NUMBER OF PAGES
		63
		15. SECURITY CLASS. (of this report)
		UNCLAS
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
13. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Batteries - Solid State Electrolytes - Interfaces - Thin Films		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>→ This report contains a</p> <p>→ Literature survey on Solid State Batteries up to December 1983.</p> <p>The Main emphasis is on solid state electrolytes. A prospective discussion is carried on Interfacial properties, Thin Films and Size Effects.</p>		

SOLID STATE BATTERIES, LITERATURE SURVEY,
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The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army.
This report is intended only for the internal management use of the Contractor and the U.S. Government.

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I. INTRODUCTION

Contemporary concern with energy sufficiency in an era of projected declining traditional energy sources has given rise to accelerated research in unconventional sources of energy and renewed interest in the improvement of traditional technologies. A particular example of such latter interest has been a growing effort in research and development of primary and secondary batteries.

Modern materials science has played a major role in this development which spans the regimes of large scale secondary power supplies for load leveling and vehicle propulsion (Visser, 1980) and low current stable primary sources for medical applications (e.g. heart pacemakers, cf. Owens and Skarstad, 1979). Research in batteries has been the traditional domain of electrochemistry and to a large extent the more specialized field of aqueous solution electrochemistry (cf. Bockris and Reddy, 1970). We shall not attempt to cover developments within this larger area but shall attempt to review a more restricted area encompassing both solid state physics and electrochemistry, that of fully solid state electrochemical systems. Our interest will be primarily secondary batteries and the progress which has been achieved in the past ten years. However, there are numerous other subfields of solid state electrochemistry in which new materials have made an impact and some reference will be made to these.

In order to gain some overall perspective regarding practical goals for research in secondary energy sources, it is pertinent to consider two major large scale applications. Tables 1 and 2 (Cairns, 1980) give estimates of battery parameters for use in off-peak energy storage and urban electric automobiles. In particular, specific energy densities of $> 70 \text{ Wh/kg}$ are desirable for urban automobile transport. This is to be compared with the value of 42 Wh/kg characteristic of the Pb/PbO_2 cell (Caulder and Simon, 1980). Reckoning with a factor of three to six for the ratio of theoretical specific energy calculated considering only the equivalent weights of cathode and anode materials) to specific energy of a practical cell (Cairns and Shimotake, 1969), figures of merit for such applications are of the order $400\text{--}500 \text{ Wh/kg}$. There are of course other factors to be considered as indicated in tables 1 and 2.

Secondary batteries may be classified according to the physical state of the three basic constituents, anode/electrolyte/cathode. Some representative examples are given in table 3. The first three classes of batteries have undergone extensive development, in particular the first classical category. We may remark certain of the drawbacks of such technologies (Murphy and Christian, 1979). For category 1, aqueous solution cells, major problems are shelf life limitations due to corrosion at the electrode-electrolyte interface and a limited operating temperature range determined by the electrolyte. The second and third categories, due to the high operating temperatures,

REQUIREMENTS OF BATTERY SYSTEMS

TABLE 1

REQUIREMENTS FOR OFF-PEAK ENERGY STORAGE BATTERIES

Discharge time	3-8 hours
Charge time	5-7 hours
Overall efficiency	> 70%
Energy/floor area (6.1 m max. height)	80 kWh/m ²
Typical size	100-200 MWh
Cycle life	2000
Lifetime	10 years
Cost	\$30/kWh

TABLE 2

REQUIREMENTS FOR URBAN ELECTRIC AUTOMOBILE BATTERIES

Specific energy	> 70 Wh/kg [*]
Energy density	>140 Wh/l
Specific power, 15 sec. peak	130 W/kg
Energy efficiency	> 70%
Cycle life, 80% DOD	>300
Lifetime	3 years
Cost	<\$70/kWh
Typical size	20-40 kWh

^{*} Corresponds to 140 km range for a battery mass of 30% of the vehicle test mass.

TABLE 3
COMMON BATTERY CONFIGURATIONS

Anode	Electrolyte	Cathode	Example
1. Solid	aqueous	solid	$\text{Cd} \text{KOH} \text{Ni}_2\text{O}_3$
2. Solid	molten salt	solid	$\text{LiAl} \text{LiCl-KCl} \text{FeS}$
3. Liquid	solid	liquid	$\text{Na} \beta\text{-alumina} \text{S}$
4. Solid	solid	solid	$\text{Li} \text{LiI} \text{I}_2$

require highly corrosion resistant components. These latter nevertheless are under development for off-peak energy storage and vehicle propulsion applications (Visser, 1980 ; Farrington and Briant, 1979 ; Kennedy, 1977). The fourth category, to which this review is addressed, is potentially superior to class one batteries due to recent development of fast ionic conducting solid electrolytes and to class two and three batteries due to the fabrication of new classes of solid cathode materials incorporating high energy density and having prospects of high reversibility. This category has its own particularities and problems, which will become clear. Its potential lies in the complete solid state nature, making such batteries advantageous where varying size, shape and temperature constraints are important. Such batteries have been the subject of increasing research in the past decade and in terms of research and development this category represents the youngest of the four.

The subject of solid state batteries has been reviewed by Liang, (1974). References to work previous to 1974 may be found there. The resurgence of interest was spurred by the discovery of highly conducting solid electrolytes in the late 1960's, in certain cases compatible with high temperature, high energy density redox couples (e.g. the β -aluminas ; Yao and Kummer, 1967 ; Kummer, 1972) and in others capable of ambient temperature operation (e.g. RbAg_4I_5 , Bradley and Greene, 1967 ; Owens and Argue, 1967). The second aspect characterizing more recent developments has been the advances made in electrode technology. In particular, ion insertion compounds which give promise of high reversibility and high energy density have received increasing attention (Whittingham, 1979). The battery applications of these and other high energy density materials have been reviewed by Murphy and Christian (Murphy and Christian, 1979).

Liang (Liang, 1974) has given a characterization of the desiderata for a battery. There are :

1. rugged construction
2. high reliability
3. long shelf life
4. High energy density
5. wide operating temperature range.

Various applications have as goals optimization of a subclass of these. Since few of the systems which we shall consider have reached the production stage, we shall be concerned mainly with question of energy density and temperature range. A pictorial summary of some current laboratory cells is given in Figure 1 which sets the scale of power and energy densities.

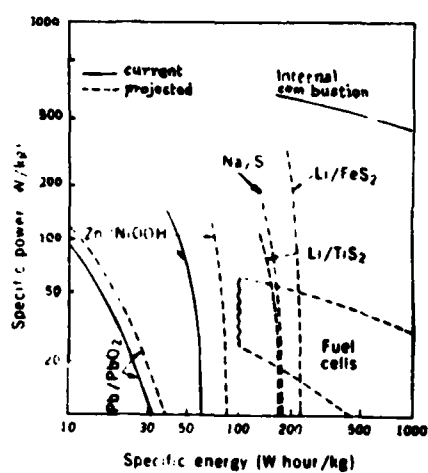
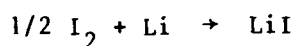


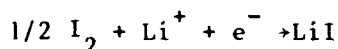
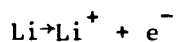
Figure 1 : Specific power and energy from some present-day energy sources and projections for the future based on (/).

From Murphy and Christian, 1979.

The present review is patterned after a generic electrochemical cell of the form anode electrolyte cathode, for example $\text{Li}|\text{LiI}|\text{I}_2$, consisting of a positive electrode (anode) at which oxydation takes place (Li is oxydized to Li^+), a negative electrode (cathode) at which reduction takes place (I_2 is reduced to 2I^-) and a solid electrolyte (in this case LiI) capable of transporting the ionic species necessary for charge neutrality (here Li^+). We shall review the solid electrolyte components, the cathode components and anode components. The equilibrium open circuit potential as is well known is determined by the change in Gibbs free energy of the overall redox couple. In the case of the $\text{Li}|\text{LiI}|\text{I}_2$ cell the overall reaction is :



the sum of the two half reactions :



with $G/N_e = -E = -2.80\text{V}$ (cf. Owens, Oxley and Sammells, 1977). In general, however, under dynamic conditions, that is to say when more than the infinitesimal currents necessary to define a thermodynamic quantity such as G are drawn, the operating voltage of a cell will be less. How much less is determined by the dynamics of charge transfer at the interface between electrolyte and anode and electrolyte and cathode. There may be equilibrium effects related to concentration dependence of the ionic chemical potential at both interfaces as well (Steele and Shaw, 1978). The subject of the structure of the electrolyte-electrode interface in aqueous electrochemistry has a long history and the rate determining processes at the interface are still not completely understood (Conway, 1977). The solid state problem is that of the metal-insulator or semiconductor-insulator interface under conditions of both electronic and ionic transfer. Much less work has been done in this field. This is understandable perhaps in view of the difficulty of obtaining a pristine interface as opposed to the case of molten or aqueous electrolytes for which one may hope to approximate uniform wetting and a well characterized interface. Nevertheless, an understanding of interface kinetics is essential to realizing the potential of solid state electrochemical systems.

The outline of this review then is as follows : Section II treats solid electrolytes. The material parameters of different classes of fast ionic conductors are reviewed. The theoretical understanding will be indicated, but the emphasis will be more materials oriented since excellent reviews exist of the theoretical situation (e.g. Dieterich, Fulde and Peschel, 1980). Section III considers the cathode materials for solid state batteries. Some emphasis is given to ion insertion compounds which have shown promise with regard to reversibility and energy density. Section IV considers the anode, the

materials for which have been typically more traditional. In Section V, we consider the interface problem, cathode-electrolyte and anode-electrolyte treating questions of compatibility and dynamics. The final Section VI is an attempt to summarize the progress made in the past ten years in assembling the above elements. We shall also indicate prospects for future development. The field of solid state electrochemistry is an interdisciplinary field encompassing solid state physics, physical chemistry and electrochemistry. This eclectic mixture has its own eclectic literature and we have made an attempt to be reasonably complete in surveying it.

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SECTION II

II. SOLID ELECTROLYTES

II.A. Anionic Conductors

II.B. Cationic Conductors

II. SOLID ELECTROLYTES

Extensive reviews of the theory and applications of solid electrolytes have appeared in the past 10 years. (See eg. van Gool 1973, Mahan and Roth 1976, Vashishta et al 1979, Hagenmuller and van Gool 1978, Bates and Farrington 1981). Generally one can classify materials with respect to the form of the transition in the conductivity as a function of temperature. This leads to a distinction between three classes of ionic conductors : Class I : those showing a discontinuous transition, Class II : those showing a continuous transition but showing a λ -like or broadened singularity in the specific heat C_p . Class III : those showing no transition but having unusually large ionic conductivity. Generic materials for three classes are respectively AgI, PbF_2 and β -alumina. The ionic conductivity in the best of cases reaches values comparable to ionic melts i.e. of the order $1-10(\Omega.cm)^{-1}$ (see Figure II-1). More pertinent to our purposes here is a more materials related division. There are many ways of doing this, however one may classify morphologically according to crystalline and amorphous ionic conductors and further the former with respect to anionic or cationic conduction, the latter with respect to glassy or polymeric composition. The more well defined crystalline conductors have received the most attention both theoretically and experimentally. The glassy and polymeric conductors are potentially more interesting with regard to miniaturization in view of their potentially more advantageous characteristics as films.

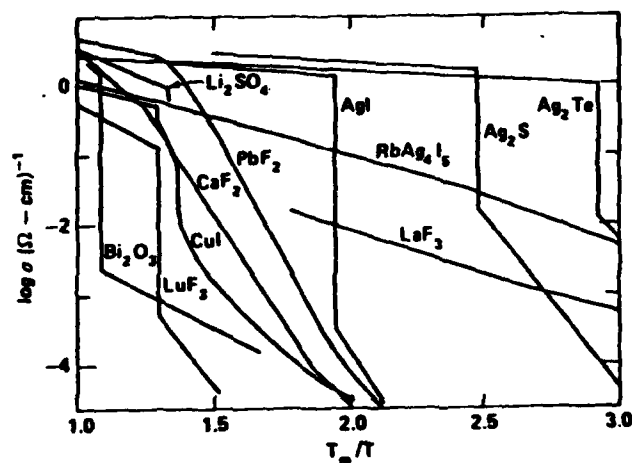


Figure II.1. : Logarithm of the conductivities of some typical superionic conductors plotted against T_m/T with T_m the melting temperature of the solid.
 From J.B. Boyce and B.A. Huberman, Phys. Rev. 51, 189-265 (1979) Fig.2-1, p.192.

II.A. ANIONIC CONDUCTORS.

Of anionic conductors the most promising class and most studied is the class of fluorine ion conductors (Réau and Portier, 1978), there are several reasons for interest in these systems. First the fluorine ion because of its high electronegativity (4.0. on the Pauling scale) and hence oxidizing potential for is a good candidate for one of the elements in a relax couple. Secondly the F^- ion because of its small size and minimal charge is the best candidate for fast ion conduction in an anionic electrolyte. A final consideration is the relatively simple crystalline structure for the more conducting of these compounds, most of which crystallize in the fluorite structure of classely related structures having similar short range order e.g. tysonite and YF_3 . The cationic coordination in these three structures is respectively 8, 9 and 11. A selection of some of the more extensively studied systems is given in Table II.1. In many cases the transition to the highly conducting phase is of type two with the inderlying cation lattice remaining unchanged. In the case of lattices with the fluorite structure, (see Figure II.2.), the cations are arranged on a fcc lattice with the fluorine ions occupying the eight tetrahedral positions in the cubic cell. Alternatively it consists of anions on a cubic lattice with cations occupying every other body centered position. Considering this structure from the point of view of the cationic lattice one sees that, in view of the fact that the cation lattice remains invariant in a type II transition, there will be a either substantial occupation of the octahedral sites or the mechanism of anion conduction must contain substantial elements of cooperative motion. We shall return to this point later.

A further aspect of the conduction process which has received little theoretical attention is the relationship of the polarizability of the cation. In a given isostructural sequence eg. PbF_2 , YF_3 and BiF_3 , the larger the cationic polarizability the larger the ionic conductivity. This is in some ways similar to the situation in the cationic conductors. The relationship between ionic polarizability and conduction has been addressed by (Pardee and Mahan, 1975) and (Mahan, 1980) within the context of small polaron theory. However, in most situations the more appropriate model is one of hopping conduction rather than band conduction and the applicability of such small polaron theory is questionable.

Thus far we have discussed stoichiometric compounds. Nonstoichiometry plays an important role in the material sciences of the fast ion conduction for the fluorite structures. The trivalent fluorides in particular form solid solutions of the form $M_{1-x}M'_xF_{2+x}$ where $M = Ca, Sr, Ba, Pb$. Tetravalent fluorides also form solid solutions (Réau and Portier, 1978 ; Wapenaar and Schoonman, 1979 ; Hagemuller, Réau, Lucat, Mater, Villeneuve, 1980). A review with further references is found in (Schoonman, 1981).

TABLE II.1.

REPRESENTATIVE FLUORIDE CONDUCTORS

	Type	Structure	T(°C)	Tmelt(°C)
PbF ₂	II	Fluorite	430	822
CaF ₂	II	Fluorite	1150	1418
SrF ₂	II	Fluorite	1180	1400
BaF ₂	II	Fluorite	960	1320
LaF ₃	II	Tysonite	---	1493
CeF ₃	II	Tysonite		1460
LuF ₃	I	Orthorhombic- hexagonal	945	1184
YF ₃	I	Orthorhombic- hexagonal	1052	1155

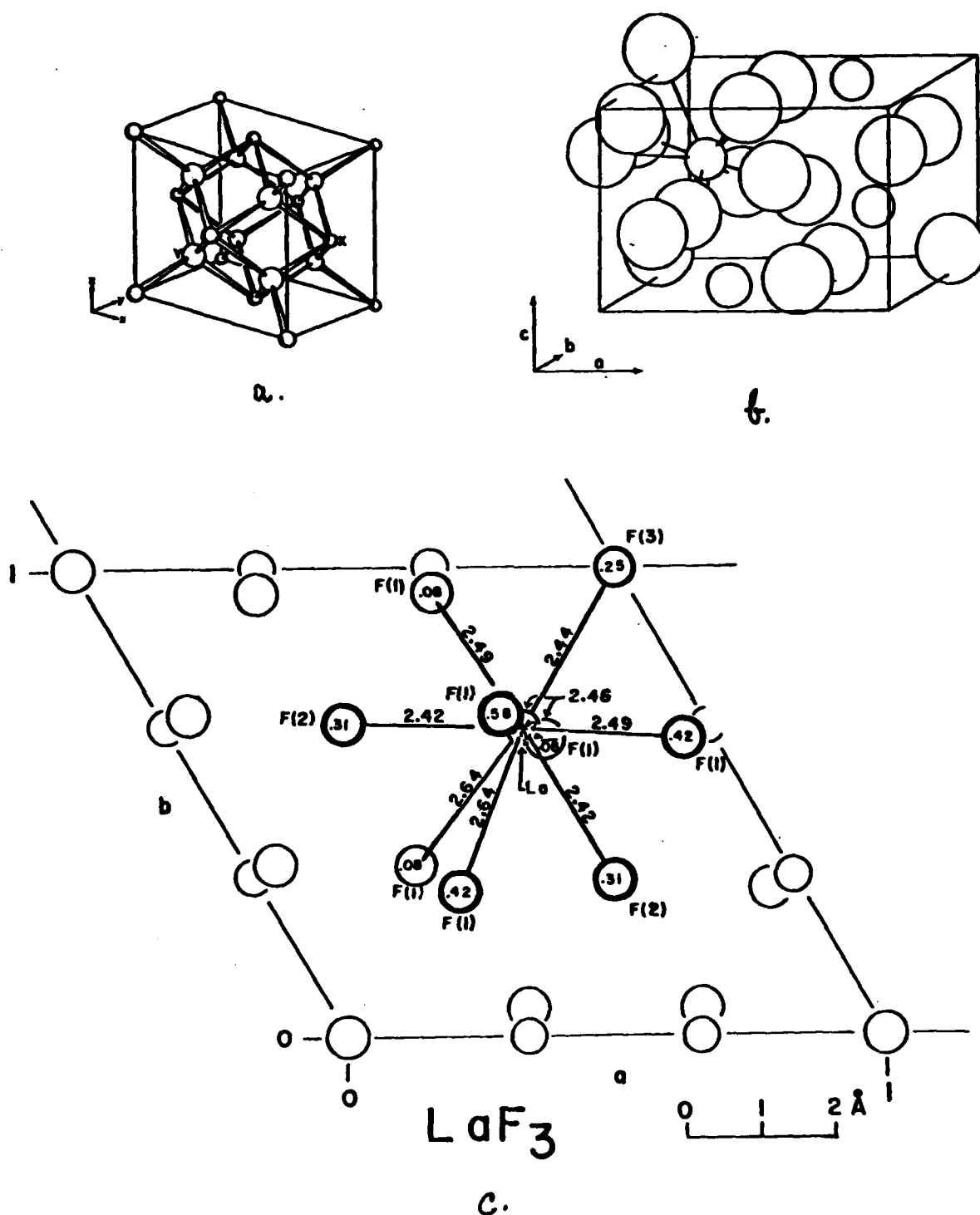


Fig. 11.2. :
 a. Fluorite structure
 b. α - YF_3 structure
 c. Tysonite structure

(Shapiro and Reidinger, 1979)
 (Zalkin and Templeton, 1953)
 (Zalkin et al, 1966)

As an example of the x dependence of the conductivity we refer to Fig.II.3. In general, the conductivity is increased with the addition of a concentration x of the tri or tetravalent fluoride and the increase is linear in x for small x . For higher concentrations the enhanced ionic motion model of (Schoonman 1979) provided some justification for the concentration dependence of the activation energy in the phenomenological formula.

$$\sigma T = A_0 \exp \left\{ - \frac{1}{kT} \left(\Delta \bar{H}_m - \frac{p^2}{4kT} \right) \right\}$$

in which a small fraction of the F^- interstitials are presumed to carry the current while the major proportion of the anion excess is assumed to be quenched into bound stable clusters. The microscopic mechanism for conduction is interpreted as a non colinear interstitialing mechanism and $\Delta \bar{H}_m$ is an average migration enthalpy and $p=C\sqrt{x}$ corresponds to the width of the interaction energy distribution function. This model has had some success in interpreting the concentration behavior of fluoride solid solutions (cf. Schoonman 1981 and Wapenaar and Schoonman, 1981).

The description of defects in the low concentration regime is possible in terms of nearest neighbor and next nearest neighbor (type I and type II) associates of the form $(M_m F_i)^x$. More complicated defect configurations are also possible and have been observed in ESR and ENDOR experiments (Catlow, 1979 ; Jacobs and Ong 1980). Static structural relaxation simulations of Catlow and coworkers (Catlow, 1982) are in general agreement with the low concentration studies of defects. Whether the enhanced ionic motion model will be justified on the basis of similar calculations remains to be seen. These systems are sufficiently complicated that in the large concentration limit such cluster calculations may be limited by size considerations.

As a theoretical digression it may be pointed out that due to the relative simplicity of the stoichiometric fluorine ion conductors, a good deal of numerical simulation work has been done on these systems. The two main methods which have been used to study the properties of the fluoride ion conductors and the fluoride structure in general from a first principles point of view have been the lattice relaxation approach (Catlow, 1980) and the molecular dynamics approach first applied to fast ion conductors by Rahman (Rahman, 1976). In the lattice relaxation approach the lattice is divided into two regions, an inner region in which the energy is computed using the lattice and defect pair potentials and an outer region treated in the spirit of Mott and Littleton (Mott and Littleton 1938) in a continuum theory modified to take into account polarizability in a shell model treatment. The result of such a calculation is relative binding

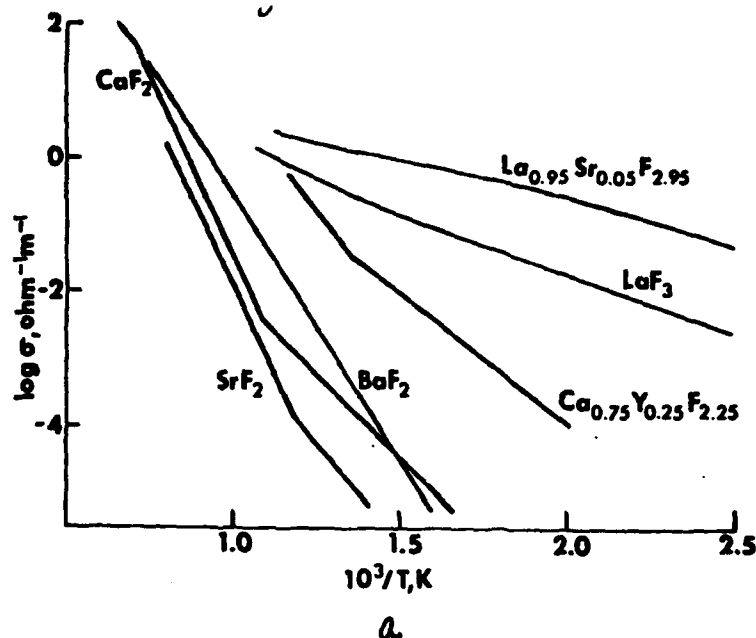


Figure II.3a. : Conductivity as a function of temperature for CaF_2 , SrF_2 , BaF_2 and LaF_3 compiled from this work and refs.8-10. From Nagel and O'Kaeffe, 1973.

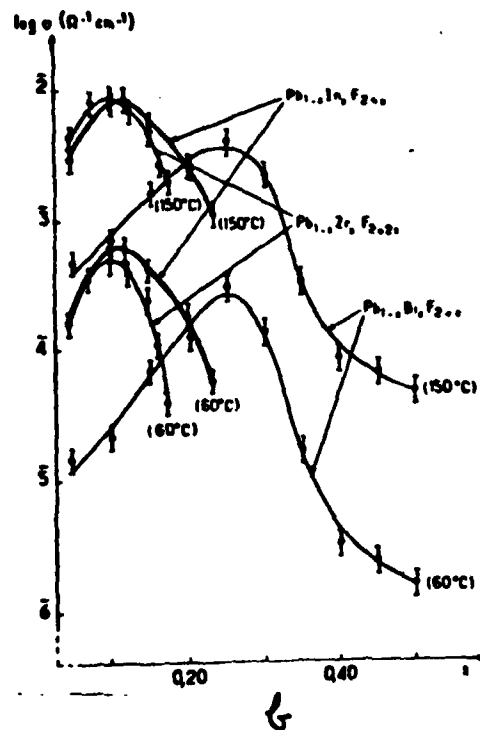


Fig. II.3b. : Isotherm of the conductivity variations as a function of the degree of substitution for the solid state solutions $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$, $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$. From Réau, Mahan, Kacim, Champarnand-Mesjard, 1982.

energies of defect clusters. In the molecular dynamics approach the classical equations of motion for a finite system with periodic boundary conditions are solved in a micro-canonical ensemble, that is to say at fixed energy corresponding to a fixed temperature. Since in principle all positions of the ions are known in a molecular dynamics experiment, in principle one should be able to give a characterization of the ionic motion which gives rise to superionic behavior. This latter presumption is in many cases illusory and there is still no simple explanation of the mechanism of conduction in the high temperature phases of the stoichiometric fluorites.

In very early treatments of fast ion conduction in the fluorites the transition in the fluorites was described in terms of an ionic sublattice melting. In view of the fluorite structure as a cubic lattice of anions with energy other body center occupied by a cation (see Fig. II.2.) this would predict a high concentration of interstitial anions. Since, however, Frenkel formation energies are of order 2-3eV. Whereas enthalpy changes at T_c are of the order 0.1eV, unless defect interactions act to lower appreciably the formation energy a more complex mechanism is indicated. One of the possibilities inherent in the static lattice simulations is the ability to study this essentially static question and simulations have shown that although the Frenkel formation energy is lowered due to defect interactions, it still remains of the order 1eV, essentially ording out a molten sublattice interpretation at least in so far as sublattice metting is construed as the statistical occupation of interstitial sites by the anions.

The work of Catlow (Catlow, 1983) and others using the static lattice defect simulation approach has done much to clarify the nature of the defect structure of the fluorite phases below T_c . The nature of defect structure in the trivalent solid solutions has indicated the usefulness of this approach as a quantitative scheme (Wapenaar and Catlow, 1981). The general picture in these systems of successive regions characterized by 1°) association-dissociation of interstitial neutrals, 2°) free defect conduction, 3°) intrinsic conduction by anion vacancies, 4°) intrinsic conduction by anion interstitials as temperature is increased to below T_c seems to account for the experimental results. (Schoonman and den Hartog, 1982). Above T_c , the situation as far as anion conduction in the fluorite phases remains somewhat controversial. Above the transition to the superionic phase the diffusion constant of the anion approaches values of the order $2.6 \times 10^{-5} \text{ cm}^2/\text{s}$ i.e. of the order of molten salts. The molecular

dynamics simulations (cf. Rahman 1976, 1978, and Gillan 1980, 1981, 1983, Dixon and Gillan, 1980) are consistent with residence times τ_Y and flight time τ_f in the ratio $\tau_f/\tau_Y = 1/10$. Moreover these same simulations show that the most prominent directions for ionic motion are along 100 directions with little octahedral occupation. Since the ratio of flight and residence times argues for a hopping picture whereas low octahedral occupancy creates a blocking effect, cooperative effects are important and analysis of some of the molecular dynamics studies (Rahman, 1978) give rise to a picture of a small concentration of highly mobile and short lived interstitial defects giving rise to a high anion diffusion coefficient presumably involving a kind of interstitial mechanism. These descriptions depend to a certain extent on the manner of analysing the motion of the anions and although the language of lattice defects is argued to be appropriate, a simple description of the cooperative behavior is lacking. The lattice statics results have offered another suggestion based upon a certain form of defect. (Catlow and Hayes, 1982) shown in Fig.II.3. This so called 2:2:2 cluster, it is assigned is formed as T_c is approached and antiFrenkel pairs begin to interact. This cluster reduces the effective Frenkel energy leading to a decreases in the formation energy. However the clusters themselves interact and it is posited that their number is stabilized by interactions leading to a finite number of interstitial defects above T_c . Whether this defect structure survives when dynamics is included has not been investigated in molecular dynamics experiments.

In summary the fluorite related anionic fast ion conductors typically reach anionic conductivities of the order $10^{-1}(\Omega.cm)^{-1}$. In the case of stoichiometric fluorite structures, the transition occurs typically at high temperatures of the order $0.8 T_{melt}$.

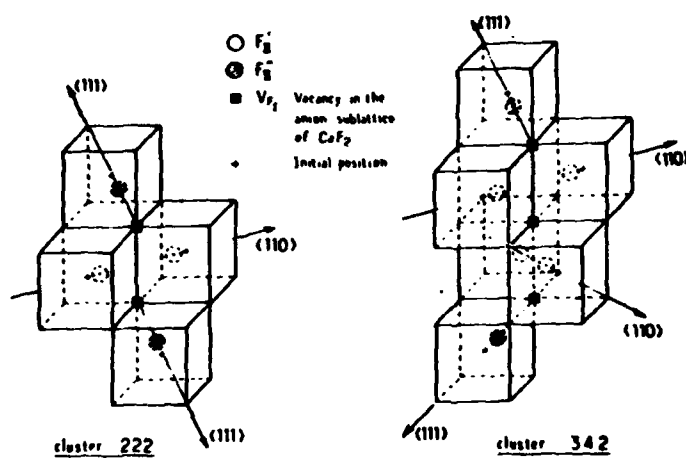
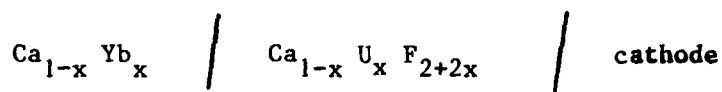


Fig. 11.4. : Defect clusters.

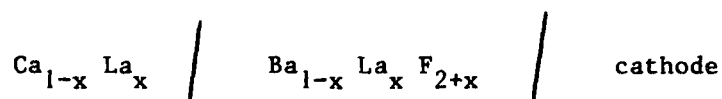
(From Réau and Portier, 1978).

This restricts these systems to high temperature applications. Binary fluorides however, form solid solutions with ternary and quaternary fluorides over a wide concentration range. The defect structure introduced has two effects. The first is to lower the transition temperature at which the Faraday transition takes place (in some cases by as much as several hundred K (c.f. Catlow et al 1979). The second is to increase the conductivity. For fixed temperatures this can lead to orders of magnitude increases in the concentrated regime. Some typical examples are illustrated in Table II.2 and Figure II.4. This fact makes possible construction of cells at lower temperatures.

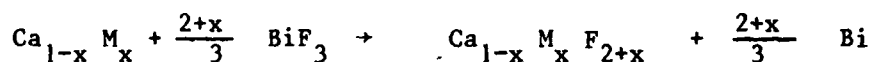
One such example has been investigated by Schoonman et al (Schoonman et al. 1979) and (Schoonman et al. 1981) and is of the form.



and



with the cathode BiF_3 or $\text{BiO}_{0.1}\text{F}_{2.8}$ and the cell reaction on discharge :



The use of the alloy anodes $\text{Ca}_{1-x}\text{Yb}_x$ reduces the anodic passivation encountered in previous cells using metallic anodes. Instead of the pure MF_2 layer being formed, the doped discharge products $\text{Ca}_{1-x}\text{M}_x\text{F}_{2+x}$ are formed whose ionic conductivity is greatly enhanced thus leading to orders of magnitude decreases in the cell resistivity as the discharge reaction proceeds.

TABLE II.2.

Compounds	σ (100°C) (Ωcm) ⁻¹	Activation energy (eV)
KBiF ₄	$4 \cdot 10^{-3}$	0.38
RbBiF ₄	$5 \cdot 10^{-3}$	0.37
α -TlBiF ₄	$3 \cdot 10^{-4}$	0.38
β -TlBiF ₄	unstable	0.30
α -PbF ₂	$2 \cdot 10^{-6}$	0.48
β -PbF ₂	10^{-4}	0.45
Pb _{0.75} Bi _{0.25} F _{2.25}	$2 \cdot 10^{-3}$	0.39

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II.B. CATION CONDUCTING ELECTROLYTES.

Cation conducting solid electrolytes are by far the most important class of solid electrolyte systems. The interest is mainly due to the large ionization potentials of the alkali metals coupled with their a small size and mass. Their size characteristics make them suitable for fast ionic conduction both in solid electrolytes and in mixed electrolyte intercalation and insertion compounds. In fact the existence of many alkali metal insertion compounds with large free energies of insertion corresponding to the most favorable cathodic energy densities has resulted in a predominance of research in cationic conductors. In this section we deal with crystalline materials. A further subdivision may be made according to the effective dimensionality of the conduction process.

II.B.1. Three dimensional structures.

Silver ion conductors

The classical example of a cationic conductor is α -AgI (Turbandt and Lorenz, 1914) stable above 420 K. This substance, although of little practical importance (i.e. the conducting species is Ag) has had a great impact on theoretical work and exemplifies what are some of the major features of ionic conductors. It is an example of a type I conductor (see Fig. II.1.) with a very simple crystal structure (see Fig. II.5) in which the Iodine ions are arranged on a bcc lattice with the Ag ions occupying pseudo-tetrahedral positions on the cube faces. In the α phase these positions are statistically occupied and diffraction experiments (Cava et al, 1979) as well as molecular dynamics simulations confirm that the main motion is along paths between to t sites. The rather large values of the Ag ion density along the paths (cf. Vashishta and Rahman, 1983) as well as the low value of the activation energy $\Delta E = 0.05$ eV from conductivity measurements combined with the large number of sites per unit cell have given rise to a more liquid like conception of the ionic motion. This is quite unlike, for example, the situation in the fluorite structure compounds for which activation energies are of the order 0.3 eV (cf. Table II.1), the number of anions per cell is equal to the number of residence sites and the ratios of time of flight to residence times is 1/10 whereas in α -AgI, it is of the order 1/3. These use some rather common features in the better cationic conductors, a large number of nearly available sites and low activation energies. In fact some of the first stochastic models of particle motion were motivated by the results for the quasi-elastic light scattering for α -AgI

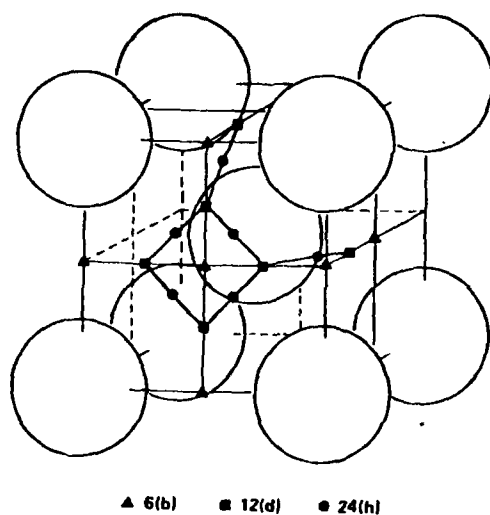


Fig. II.5. : α -AgI. (From Boyce and Huberman, 1979).

(cf. Geisel 1979). For a more complete discussion of the density distribution and local order of the Ag ions deduced from neutron diffraction, X-ray diffraction and EXAFS the review of Boyce and Huberman may be consulted (for more recent results. See Cava, Fleming and Rietman 1983). Interesting related compounds are Ag_2S and Ag_2Se which in the fast ion conducting phase have a metalloid sublattice which is, as for the iodine lattice in $\alpha\text{-AgI}$, bcc. The liquid-like properties of these systems are even more pronounced (Höch et al, 1983). These systems, however, are mixed conductors with an appreciable electronic conductivity.

By combining AgI with other compounds other fast ion conductors have been synthesized e.g. Ag_3SI , $3\text{AgI} : \text{Ag}_2\text{MoO}_4$, $4\text{AgI} : \text{Ag}_2\text{MoO}_4$. A sampling of these compounds is given in Table II.3. The above mentioned compounds are characterized by rather simple crystal structures. A more complex arrangement is found in the class of compounds MAg_4I_5 ($\text{M} = \text{Rb}, \text{K}, \text{NH}_4$). The most well known of these compounds RbAg_4I_5 discovered early on and independently by Bradley and Greene, and Owens and Argue (Bradley and Greene, 1967 ; Owens and Argue, 1967) is characterized by phase transitions at 122 K and 209 K. The high temperature α -phase has held the record for the greatest room temperature silver ion conductivity with a value $\sigma(\text{RT}) = 0.27 (\Omega\text{cm})^{-1}$ (cf. Owens, 1971). The β - α transition first observed by Geller (Geller, 1967) is an almost second order phase transition and is one of the few superionic conductors of class II for which a rather complete analysis of the critical indices has been made (Salamon 1979, 1977, 1976 Vargas et al, 1976, 1978, Salomon and Huang, 1979). An idea of the increase in complexity of the α -phase structure is given by Fig. II.6. The unit cell is characterized by 56 sites available for the 16 Ag^+ ions. Geller (Geller, 1977) designates these as the 8 Ag(c) sites, 24 Ag (II) and 24 Ag (III) sites. The Ag (II) and Ag (III) sites are connected by face sharing tetrahedra which can be considered as forming non-rectilinear channels for conduction. Despite its high value of conductivity, the activation energy for diffusion is larger than that of $\alpha\text{-AgI}$, $\Delta E(\text{RbAg}_4\text{I}_5) = 0.12\text{eV}$ (Brinkmann et al, 1979). This indicates that a jump diffusion model is more likely appropriate to this system. This interpretation is consistent with the inelastic and quasi-elastic neutron scattering (Shapiro and Salamon, 1979), low frequency Raman (Gallagher and Klein, 1979) and Brillouin (Field, Gallagher and Klein, 1978) data.

In many ways RbAg_4I_5 exemplifies the problems encountered with solid electrolytes when used in battery applications.

TABLE II.3.
SILVER ION CONDUCTORS

Compounds	T (°C)	σ ($\Omega \cdot \text{cm}$) ⁻¹
$\alpha\text{-AgI}$	147	1.3
$\alpha\text{-Ag}_2\text{S}$	200	3
$\alpha\text{-Ag}_2\text{Se}$	150	2.7
$\alpha\text{-Ag}_2\text{Te}$	160	0.7
Ag_3SI	25	0.01
$\text{Ag}_{19}\text{P}_2\text{O}_7\text{I}_{15}$	25	0.09
$\text{Rb Ag}_4\text{I}_5$	25	0.27
$(\text{Ag}_2\text{Se})_{0.925} (\text{Ag}_3\text{PO}_4)_{0.075}$	25	0.1
$((\text{CH}_3)_4\text{N})_2 \text{Ag}_{13} \text{I}_{15}$	25	0.04
$(\text{Ag}_2\text{S})_{0.50} (\text{Ag}_{1.7}\text{Te})_{0.45} (\text{Ag}_3\text{PO}_4)_{0.05}$	25	0.25
$\text{Py Ag}_5 \text{I}_6$	25	0.08

From (Takahashi, 1979) and (Geller, 1977).

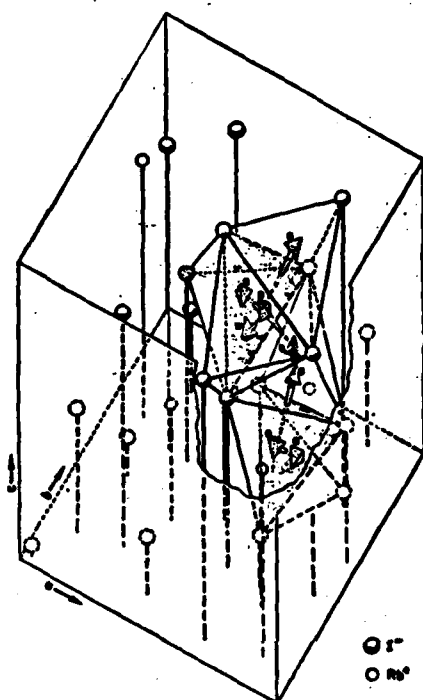
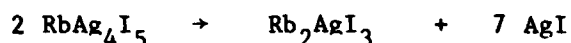


Fig. II.6. : Perspective drawing of iodide and Rb⁺ ion arrangement. Some of the shared tetrahedron faces and diffusion steps are shown. The small tetrahedra designate the Ag⁺ sites associated with the larger tetrahedra. (From Geller, 1967).

These problems and some of their solutions are chronicled by Owens et al (B.B. Owens et al, 1977). To mention the most salient of these, below 27°C the compound RbAg_4I_5 is unstable relative to the disproportionation (Topol and Owens, 1968).



both of which products have resistivities 10^5 greater than RbAg_4I_5 . This is also true of KAg_4I_5 at 36°C. Kinetic effects are such that this decomposition is hindered, however, and practical cells can be developed. The decomposition potential of the electrolyte is also rather low however (0.66eV). This restricts the energy densities which are available to redox couples. Moreover although the I diffusion rate is low it is not zero and the use of iodine cathodes gives rise to self discharge problems. These drawbacks are not insurmountable (Owens et al, 1977). However, low energy densities have prevented practical applications. (Owens et al 1983).

One of the characteristics of silver ion conductors is the existence of face sharing of tetrahedra or octahedra. Combinations of AgI with more complex molecules to construct systems having this more open "channel" structure has met with some success. Tetra-alkylammonium iodide solid electrolytes form a class of such compounds with $((\text{CH}_3)_4\text{N})_2\text{Ag}_{13}\text{I}_{15}$ as a representative form (Owens, 1970). The pyridinium ion $(\text{C}_5\text{H}_5\text{NH})^+$ also performs a similar function (Geller and Owens, 1972 ; Hibma and Geller, 1977) giving rise to octahedral channels. Some idea of the complexity of such structures can be gotten from Fig.II.7, where a view of $(\text{C}_5\text{H}_5\text{NH})\text{Ag}_5\text{I}_6$ is given. Besides these techniques for changing the characteristics of AgI based electrolytes by incorporation of foreign anions and cations (cf. Takahashi, 1979) and doping with monovalent anions to change the structural properties and decrease first order transition temperatures have been used (Bazan et al, 1982). Nevertheless, it is a truism that the ideal silver electrolyte has yet to be found.

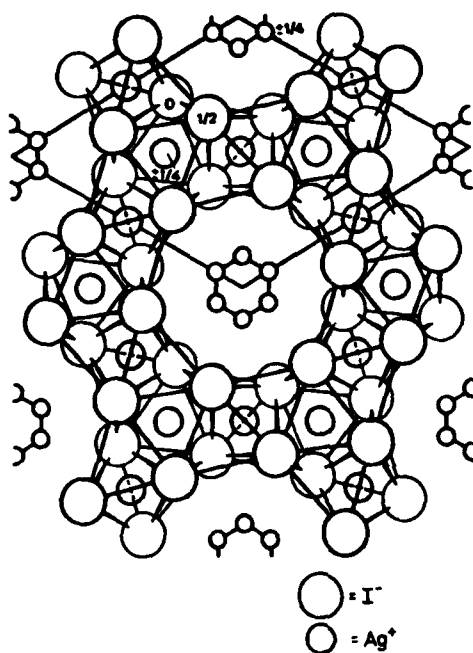


Fig. II.7. : Plan view of structure of PyAg_5I_6
 at -30°C , at which temperature
 the Ag^+ ions are ordered. (From Geller, 1977).

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Copper ion conductors.

Copper ion conductors show many of the same structural properties as silver ion conductors. The archetypical example is CuI which undergoes two phase transitions in the solid state at 369°C and 407°C. The low temperature zincblende structure achieves a rather high conductivity of $0.1 (\Omega\text{cm})^{-1}$ before transforming to a hexagonal wurtzite phase with a small discontinuity in σ . The final transformation to the α -phase is first order with the conductivity approaching $1 (\Omega\text{cm})^{-1}$ (Wagner and Wagner, 1957 ; Jow and Wagner, 1978). The α -phase is characterized by a statistical occupation of all 8 tetrahedral sites in the cubic unit cell (cf. Fig.II.8). The iodine background lattice forms a face centered structure, unlike the bcc α -AgI. Had there not been an intervening wurtzite phase, the transition from the zincblende to α -phase would have constituted a second order transition in the Landau sense. The average copper ion density in the α -phase is concentrated at the tetrahedral positions. However, there is non-negligible weight along tetrahedral-octahedral paths (Boyce and Huberman, 1979, Vashishta and Rahman, 1979). Thus even though the activation energy for conductivity in the α -phase is rather high $\Delta E = 0.2\text{eV}$ (Boyce and Huberman, 1977 ; Jost, 1960) a more liquid-like picture of the particle motion has evolved (cf. Boyce and Huberman, 1979) although interpretations of the low frequency light scattering have also been given in terms of jump diffusion (Nemanich et al, 1979 ; Dieterich and Peschel, 1983).

Due to Cu^+ ionic size considerations, there are fewer Cu compounds isostructural with AgI compounds. Oxidation is also a problem (Geller, 1977). Nevertheless, the highest conductivity at room temperature for a solid electrolyte is observed in the copper ion compound $\text{Pb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ with $\sigma(\text{RT}) = 0.34 (\Omega\text{cm})^{-1}$ (Takahashi, 1976 ; 1979 ; Takahashi et al, 1973, Kleitz et al, 1980, Geller et al, 1979). Some of the better of these compounds are listed in Table II.4.

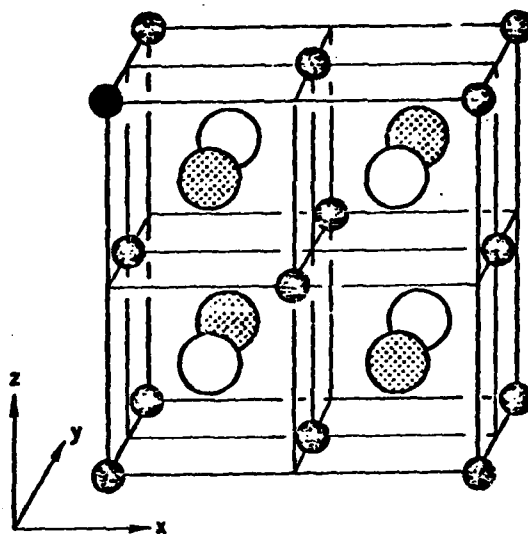


Fig. II.8. : Structure of the zincblende and α' phase of CuI. The small solid circles, at the face-centered sites, are I ions. The cross-hatched circles are Cu ions in a perfect zincblende structure at $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$. If the Cu ions are randomly distributed over the cross-hatched and open circles, one has the proposed α' phase. (From Burns et al 1979).

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TABLE II.4.

SELECTED COPPER ION CONDUCTIVITIES

Compound	T (°C)	σ (Ωcm) ⁻¹
$\alpha\text{-CuI}$	435	0.25
Cu_2S	400	0.2
$\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$	25	0.004
$\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$	25	0.34
$31\text{CuBr} \cdot 4\text{C}_6\text{H}_{12}\text{N}_4\text{CH}_3\text{Br}$	25	0.024
$37\text{CuBr} \cdot 3\text{C}_6\text{H}_{12}\text{N}_2\text{2H}_3\text{Br}$	25	0.034

From (Takahashi, 1979) and (Jow and Wagner, 1978).

Lithium ion conductors.

Lithium ion conductors form an extremely important class of solid electrolytes. This interest is due to the fact that lithium with its high ionization potential is also one of the lightest of elements. Hence redox couples giving a large free energy change (of order 3eV) result in high energy densities. This fact, however, is detrimental to the diffusion of the Li^+ ion in electrolytes. The interactions with constituents in typical non-conducting crystals are much stronger for Li^+ ions than Ag^+ or Cu^+ resulting in higher potential barriers to diffusion. This circumstance is apparent in Fig. II.9. in which representative lithium ion solid electrolyte conductivities versus temperature are shown, most of which lie three orders of magnitude below the values for copper and silver ion conductors (Weppner, 1981). LiI which is a standard in the field due to its use in the low drain cells for cardiac pacemakers has a conductivity of only $2 \times 10^{-7} (\Omega\text{cm})^{-1}$ at room temperature (Jackson and Young, 1969). The conductivity of LiI may be enhanced by a factor of 100 by the addition of fine alumina or SiO_2 particles (Liang, 1973 ; Liang et al, 1978) and it is probable that the enhancement in conductivity is due to rapid ion transport along interfaces and imperfections caused by the alumina particles (Phipps et al, 1981 : Phipps and Whitmore, 1983). LiI reacts readily with water vapor and has been shown to form both mono and trihydrates (Rudo et al, 1980 ; Pack et al, 1980 ; Poulsen, 1981). For the case of the monohydrate there is an approximate order of magnitude increase in the conductivity before the melting temperature of 128°C , although the conductivity measurements vary from worker to worker due to the difficulties of preparing and storing single phase materials. The conductivity increase for the trihydrate ($T_M = 70^\circ\text{C}$) is more modest. (Weppner, 1981). From the studies of the hydrates of LiI , there is agreement that the conductivity enhancement in $\text{LiI-Al}_2\text{O}_3/\text{SiO}_2$ systems cannot be due to formation of these compounds .

Nakamura and Goodenough (Nakamura and Goodenough, 1982a) have studied the conductivity enhancement in LiBr monohydrate with dispersed Al_2O_3 particles finding an order of magnitude conductivity enhancement at 100°C . In composite systems containing LiBr dihydrates and a second phase of monohydrate or dispersed Al_2O_3 particles, they observed an increase of two orders of magnitude above the melting temperature of the dihydrate ($T_m = 43^\circ\text{C}$) with $\sigma = 0.1 (\Omega\text{cm})^{-1}$ at 130°C . The second phase acts to demobilize the molten $\text{LiBr} \cdot 2\text{H}_2\text{O}$ however, resulting in a brittle composite which is stable against Li_xTiS_2 albeit with a low decomposition potential of 0.75 V at 55°C . These latter interesting systems have potential uses in electrode fabrication. (Nakamura and Goodenough, 1982 b).

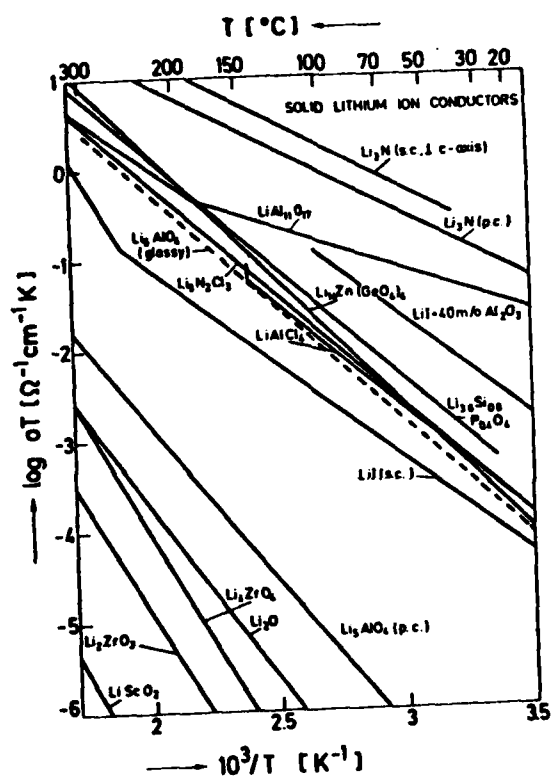


Figure II.9. : Lithium conductors.

(From Weppner, 1981).

TABLE II.5.

Lithium solid electrolytes

Compound	$\sigma(\Omega\text{cm})^{-1}$	T(°C)	Ref
LISICON	10^{-6}	RT	(1), (2)
LiI	2×10^{-7}	28	(3)
LiI - H ₂ O	1.2×10^{-5}	28	(3)
Li _{3.4} (As _{.6} Si _{.4})O ₄	2×10^{-6}	20	(4)
LiAlCl ₄	3×10^{-5}	100	(5)
	9.5×10^{-7}	25	(5)
LiFeCl ₄	5.43×10^{-7}	25	(6)
LiBr.H ₂ O	1×10^{-5}	20	(7)
LiI - Al ₂ O ₃	6×10^{-5}	25	(8)
Li _{3.3} V _{0.7} Si _{0.3} O ₄	1×10^{-5}	RT	(9)
Li _{3.5} V _{0.5} Ge _{0.4} Si _{0.1} O ₄	1.3×10^{-5}	RT	(9)
Li - β Alumina	2.4×10^{-3}	25	(10)
Li ₃ N	2×10^{-4}	RT	(11)

Ref :

- | | |
|-----------------------------------|----------------------------------|
| (1) Ohtsuka and Yamaji, 1983 | (8) Poulsen et al, 1983 |
| (2) Hong, 1978 | (9) Chen et al, 1983 |
| (3) Phipps et al, 1981 | (10) Briant and Farrington, 1981 |
| (4) Khorassani and West, 1982 | (11) Lapp et al, 1983 |
| (5) Weppner and Huggins, 1980 | |
| (6) Palvadeau et al, 1982 | |
| (7) Nakamura and Goodenough, 1982 | |

Other three dimensional compounds of current interest are "LISICON $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ " (Hong, 1978), a framework structure composed of $(\text{Li}_{11}\text{Zn}(\text{GeO}_4)_4)^{3-}$ units with the remaining 3 Li^+ ions in interstitial sites. Solid solutions based on the components $\text{Li}_4\text{SiO}_4 - \text{Li}_3\text{AsO}_4$ have also been investigated by Khorassani and West (Khorassani and West, 1982) where a description of the structural relationships to related compounds are given. These compounds show a room temperature conductivity comparable to LISICON with no aging effects such as have been observed in LISICON systems. A further generalization of the LISICON family has been studied by Kamphorst and Hellstrom (Kamphorst and Hellstrom, 1980) who consider the solid solutions $\text{Li}_4\text{GeO}_4 - \text{LiZnGeO}_4 - \text{Li}_3\text{PO}_4$. At high temperatures LISICON and $\gamma_{\text{II}} - \text{LiPO}_4$ are isostructural. Solid solutions are hence expected to be stable and the conductivity for intermediate concentrations is somewhat better than LISICON. Pseudo ternary systems of the form $\text{Li}_4\text{GeO}_4 - \text{Li}_4\text{SiO}_4 - \text{Li}_3\text{VO}_4$ have also been investigated showing similar increases in conductivity (Chen et al, 1983).

Another interesting class of compounds are the chloro-aluminates (Weppner and Huggins, 1977, 1980). LiAlCl_4 is representative and exhibits a lithium ion temperature conductivity of $3 \times 10^{-5} (\Omega\text{cm})^{-1}$ at 100°C . Related systems LiFeCl_4 (Palvadeau et al, 1982) and $\text{LiAl}_x\text{Fe}_{1-x}\text{Cl}_4$ (Palvadeau et al, 1983) show similar behavior and among these solid solutions, the compositions $\text{LiAl}_{0.25}\text{Fe}_{0.75}\text{Cl}_4$ and $\text{LiAl}_{0.75}\text{Fe}_{0.25}\text{Cl}_4$ seem to be optimal. A representative selection of Li ion conductors is given in Table II.5.

It is to be noted that except for the exceptional case of Li_3N which has a conductivity of order $10^{-3} (\Omega\text{cm})^{-1}$ at room temperature, all of these compounds have conductivities $\lesssim 10^{-5} (\Omega\text{cm})^{-1}$. This introduces limitations on the sizes of electrolyte material to be used in cells requiring high energy and current densities. Li_3N in which the conduction has two dimensional aspects will be treated in the next section.

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II.1B.2. Two Dimensional Structures

Among two dimensional cationic conductors by far the most interest has concentrated on the family of β -aluminas. The study of this material over the past ten years and its various modifications amounts to a large proportion of the work on solid electrolytes. Since for the most part, due to interfacial characteristics, these systems have been discussed mainly in terms of high temperatures as solid electrolyte separators in molten electrode high energy density cells, we omit a discussion of the properties of the conduction in this material except to note that the microscopic mechanism of conduction with regard to cooperative effects among the diffusing ions is still a subject of some controversy. A review of the β -aluminas may be found in (Kennedy 1977), and more recently (Wang et al, 1981). With regard to the lithium conducting electrolytes Li β -alumina (single crystal) shows one of the highest room temperature conductivities with $2-4 \times 10^{-3} (\Omega\text{cm})^{-1}$ to $4 \times 10^{-3} (\Omega\text{cm})^{-1}$ depending sample preparation via ion exchange with Na β -alumina (Briant and Farrington, 1981). These measurements were complex impedance measurements in the range $10^2 - 10^7$ Hz and are considerably higher than previous results (Whittingham and Huggins, 1972). A comparison of various Li ion conductors with Li β -alumina is given in Fig.II.10.

Other classes of two dimensional ionic conductors include the β and β -gallates $M - \beta - \text{Ga}_2\text{O}_3$, $M = \text{alkali metal}$ (Chandrashekar and Foster, 1977) with properties similar to the β -aluminas. Silver pyridinium compounds also exist in a two dimensional layered form $\text{Py}_5\text{Ag}_{18}\text{I}_{23}$ (Geller and Skarstad, 1974, Geller et al, 1975) although with a much reduced conductivity compared with PyAg_5I_6 (cf. Table II.3.). The silver compound AgCrS_2 (Hibma, 1980 ; Hibma et al 1981 ; Hibma, 1983) is layered and exhibits an interesting order-disorder transition at 673 K to a highly conducting phase with $\sigma \sim 0.3 (\Omega\text{cm})^{-1}$. The selenide AgCrSe_2 exhibits similar properties (Boukamp and Wieggers, 1983) with $T_c = 473\text{K}$. The latter, however, is a mixed conductor with p-type semiconducting properties. Layered structures of the form $\text{K}_{0.72}(\text{L}_{0.72}\text{M}_{0.28})\text{O}_2$ ($\text{L} = \text{In, Sn} ; \text{M} = \text{Zr, Hf, Sn}$) have been investigated by (Delmas et al, 1976) and $\text{Na}_{0.5}\text{In}_{0.5}\text{Zr}_{0.5}\text{S}_2$ by (Rouxel, 1977). These above, 250°C , show alkali conductivities similar to sintered β -aluminas.

One of the most important of the layered ionic conductors in view of Li battery research is the Li^+ conductor Li_3N . (Boukamp and Huggins, 1976). The crystal structure consists of Li_2N layers connected by Li ions forming N-Li-N bridges (Zintl and Brauer, 1935). (Rabenau and Schulz, 1976). A representation of this structure is given in Figure II.11.

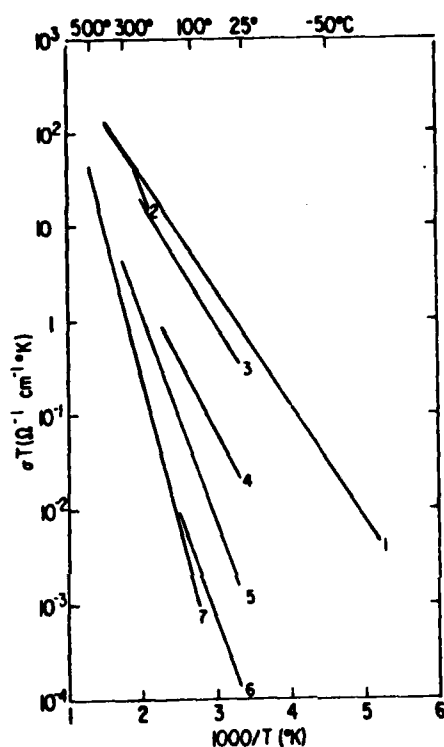


Fig.II.10. : The conductivities of various lithium solid electrolytes.

1. Lithium beta alumina
2. Lisicon (12).
3. Li_3N (1c axis) (13).
4. LiI 50m/o Al_2O_3 (14).
5. $\text{Li}_{0.8}\text{Zr}_{1.8}\text{Ta}_{0.2}(\text{PO}_4)_3$ (15).
6. LiI (16).
7. 20m/o Li_5AlO_4 + 80m/o Li_2SO_4 (17).

From (Briant and Farrington, 1981).

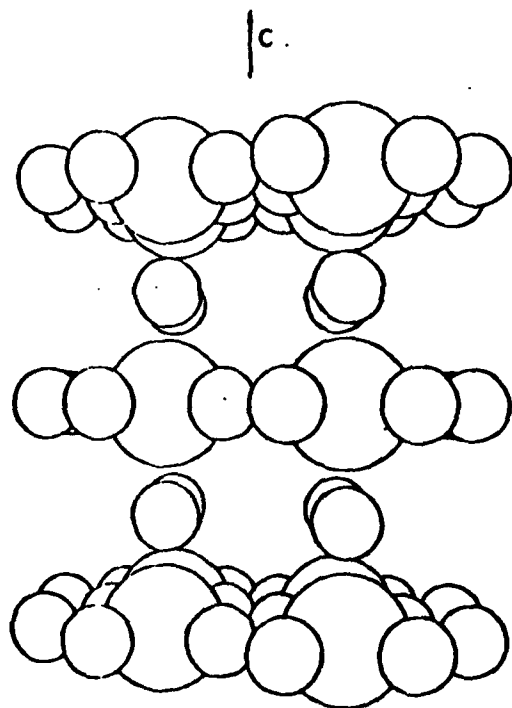


Figure II.11. : Li_3N structure showing layers
of Li(2) and N ions with bridging
Li(1) ions.
From (Lapp et al, 1983).

The history of Li_3N is of some interest (Lapp et al, 1983). The realization that Li_3N might be one of the best lithium ionic conductors occurred roughly thirty years after the initial conductivity measurements of Madsdupuy et al (Gallais et al, 1948 ; Madsdupuy, 1957). The original measurements on powders gave room temperature values of conductivity $5 \times 10^{-12} (\Omega\text{cm})^{-1}$. The measurements of Boukamp and Huggins on pressed sintered pellets gave $3 \times 10^{-7} (\Omega\text{cm})^{-1}$. The conductivity of sintered pellets annealed in N_2 at 750°C gave a further increase to $\sigma (25^\circ\text{C}) = 2 \times 10^{-4} (\Omega\text{cm})^{-1}$ with an activation energy of $E_{\text{act}} = 0.19\text{eV}$ (Huggins, 1977). Single crystal measurements by von Alpen et al (von Alpen et al, 1977 ; 1979), showed anisotropic conduction with conductivities perpendicular to the c-axis of the order $10^{-3} (\Omega\text{cm})^{-1}$ with $E_a = 0.25\text{eV}$. (Wahl, 1979), however, pointed out that all samples probably contained hydrogen as an unavoidable impurity and that this acted to increase the conductivity. A systematic study of the dependence of the conductivity on hydrogen concentration, concurrently monitoring the infrared absorption of the N-H stretching mode, has been carried out by Lapp, Hooper and Shaarap (Lapp et al, 1983 ; Hooper et al, 1979) the increase in conductivity and decrease in activation energy with increasing concentration are shown in Table II.6. These results give a value for the room temperature conductivity of $6 \times 10^{-3} (\Omega\text{cm})^{-1}$ at the highest concentration. Intrinsic values are of the order $2 \times 10^{-4} (\Omega\text{cm})^{-1}$. The actual microscopic conduction mechanism (presumably vacancy limited) has not been understood although there are arguments for bond softening upon addition of hydrogen (Lapp et al, 1983). The positions of the dopant hydrogen are found at $\sim 1\text{\AA}$ from the N in the Li_2N plane in hexagonal coordination (Thomas and Tellgren, 1981). It is agreed upon that the conduction is mainly via a hopping mechanism in the Li_2N plane between Li(2) in plane sites with the bridging Li(1) ions mainly immobile (Brinkmann et al, 1981, Schulz and Zucker, 1981, Zucker and Schulz, 1982). In the hydrogenated samples, however, there is the added complication of a small H^+ conductivity (von Alpen and Bell, 1981 ; Bell and von Alpen, 1981 ; Bell and Armstrong, 1981).

One of the shortcomings of Li_3N as a lithium solid electrolyte is its low thermodynamic decomposition potential $\Delta G = 0.44\text{V}$. In practical applications kinetic constraints may make this less of a problem (Knutz and Skaarup, 1983). However, efforts have been made in forming pseudo-binary compounds for which the second component (eg. LiCl) has a higher stability. $\text{Li}_{1.8}\text{N}_{0.4}\text{Cl}_{0.6}$ (Rabenau, 1982 ; Sattlegger and Hahn, 1971) is one of these and although its room temperature conductivity is lower by an order of magnitude, it has a greater stability and a comparable conductivity beyond 250°C .

TABLE II.6.

Relative H concentration	A_0	$\sigma(25^\circ\text{C})$ $(\Omega.\text{cm})^{-1}$	E_a (eV)
0.24	1600	1.9×10^{-4}	0.263
0.45	3300	5.1×10^{-4}	0.256
1.00	6400	2.8×10^{-3}	0.229
1.22	5400	2.8×10^{-3}	0.225
1.8	4000	6×10^{-3}	0.198

$$\sigma T = A_0 \exp(-E_a/kT).$$

From Lapp et al, 1983.

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II.B.3. Quasi one dimensional conductors :

Quasi one dimensional solid electrolytes while not of direct interest practically, are interesting systems with regard to the confrontation of theory with experiment. In general one-dimensional models can deal with all the complications of stochastic interactions, background lattice potentials and pair interactions among mobile particles. Two of the most studied systems are Hollandite $K_{2y}^{+}(Mg_y Ti_{8y} O_{16})^{2y-}$ (Takahashi and Kawahara, 1974) and β -Eucryptite ($LiAlSiO_4$) (von Alpen et al, 1977). A neutron diffraction map of the latter is given in Fig.II.12, (Guth and Heger, 1979) to emphasize the dimensionality of phase systems β -Eucryptite exhibits high values of Li ion conductivity and strong conductivity asymmetry $\sigma_{\perp}(600^{\circ}C)=2 \times 10^{-4} (\Omega cm)^{-1}$, $\sigma_{\parallel}(600^{\circ}C)=10^{-1} (\Omega.cm)^{-1}$ (von Alpen et al, 1977). The interesting NMR properties are treated in (Schweichert et al, 1983) and neutron quasi-elastic scattering by (Bernotat et al, 1983; Radons et al., 1983). A review of the theories concerning the dynamics of excitations in these systems may be found in (Dieterich et al, 1980).

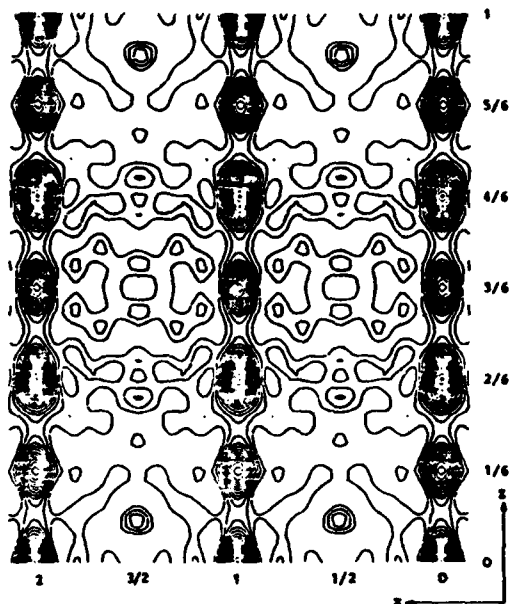


Figure II.12. : Contour plot of a difference Fourier map of the high temperature modification. The $a - c$ section of the map at $y = 0$ is plotted. Only negative contour lines are shown for illustrating the Li distribution. β -encryptite from (Guth and Heger, 1979).

Quasi one dimensional systems. Ref.

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III. INTERFACIAL PROPERTIES THIN FILMS AND SIZE EFFECTS

There are several parameters which specify the size dependent properties of solid electrolyte electrochemical systems. Among these we may mention the size of the electrolyte itself, the size of the cathode and the size of the active cathode particles if the cathode is prepared in the form of a dispersed electrode. One advantage of solid electrolyte systems is that in a planar geometry the perpendicular dimension may be decreased to potentially very small dimensions thus decreasing the internal cell resistance. Experimental limits have not been completely investigated for this point. However, recent experimental results using boro-silicate glasses are promising. Although the room temperature conductivities of these glasses are low ($\sim 2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$) the stability range is rather high of order 4.5V. Since it is resistance which is important, conductivities in this range are not obstacles provided thin enough films are used. Thin film batteries have been fabricated (Couturier et al, 1983) by sputtering boro-silicate glasses on electrodeposited TiS_2 layers giving cell emf's of 2.45V at $5 \mu\text{A}/\text{cm}^2$. Typical film thicknesses of order μm are possible. In such systems (Couturier et al, 1983) interfacial quality appears to be the major problem.

with M = metal, C = cathode, E = electrolyte, A = anode and we assume that C is an intercalation electrode with the intercalation planes normal to the layer and which on discharge intercalates A^+ ions which are conducted by the solid electrolyte E. The metal electrodes are assumed blocking to A^+ . This is a highly idealized example, since typical transition metal dichalcogen crystals are formed in flakes with the in plane dimension the longer. If we consider only the cathode the electronic and ionic currents j_e and j_i are related to the gradients of the electrochemical potentials $\bar{\mu}_e$, $\bar{\mu}_i$ via :

$$j_e = \frac{\sigma_e}{e} \nabla \bar{\mu}_e$$

$$j_i = \frac{-\sigma_i}{e} \nabla \bar{\mu}_i$$

Defining an emf ϵ as

$$\epsilon = -(\bar{\mu}_e + \bar{\mu}_i) \text{ gives}$$

$$e \left(\frac{j_i}{\sigma_i} - \frac{j_e}{\sigma_e} \right) = \nabla \epsilon$$

and using the continuity equations :

$$\nabla \cdot j_i + \frac{\partial \rho_i}{\partial t} = 0$$

$$\nabla \cdot j_e + \frac{\partial \rho_e}{\partial t} = 0$$

these equations give a diffusion equation for $\epsilon(x)$

$$\nabla^2 \epsilon = e \nabla \cdot \left(\frac{1}{\sigma_i} j_i - \frac{1}{\sigma_e} j_e \right)$$

In general σ_i and σ_e depend on concentration, but for the purposes of estimates we assume constant values. (The more general case is treated by Heyne and den Engelsen, 1977).

For the concentration dependence of the chemical diffusion coefficient of TiS_2 and TaS_2 see (Basu and Woroell, 1979)).

In that case

$$\begin{aligned} \nabla^2 \epsilon &= e \left| \frac{1}{\sigma_i} \nabla \cdot j_i - \frac{1}{\sigma_e} \nabla \cdot j_e \right| \\ &= e \left| \frac{1}{\sigma_e} \frac{\partial \rho_e}{\partial t} - \frac{1}{\sigma_i} \frac{\partial \rho_i}{\partial t} \right| \end{aligned}$$

which, since $\rho_i = -\rho_e = en$, becomes

$$\nabla^2 \epsilon = -e^2 \left| \frac{1}{\sigma_i} + \frac{1}{\sigma_e} \right| \frac{\partial n}{\partial t}$$

or defining a chemical diffusion coefficient in the usual way, namely

$$\tilde{D} \equiv -\frac{\sigma_i}{e^2} \frac{d\sigma}{dn}$$

we have

$$\tilde{D} \nabla^2 \epsilon = \sigma_i \left| \frac{1}{\sigma_i} + \frac{1}{\sigma_e} \right| \frac{\partial \epsilon}{\partial t}$$

In the example under consideration, i.e. intercalation electrodes, $\sigma_i \ll \sigma_e$ and the decay of emf is governed by the diffusion equation

$$\tilde{D} \nabla^2 \epsilon = \frac{\partial \epsilon}{\partial t} .$$

Without solving this equation (the solution of which depends on the initial $\epsilon(x,t)$ distribution) it is clear that, if the dimension of the electrode in the normal direction is l , the time constant of the system will be $\tau = \frac{l^2}{\tilde{D}}$. Since for the better intercalation compounds (e.g. TiS_2 , TaS_2 cf. Basn and Wornell, 1979) \tilde{D} can be as large as $\sim 10^{-7} \text{ cm}^2/\text{sec}$ we have time constants of order $\tau \sim N^2 10^{-8} \text{ sec}$ where N is the number of film layers taking a typical layer as having a thickness $\sim 3\text{\AA}$. Thus, large discharge rates are favored by small thicknesses and one can think of intercalating this basic structure as a series of layers. The power per unit area for such a structure, assuming a cathode energy density of $\sim 500 \frac{\text{Wh}}{\text{kg}}$, appropriate Li_xTiS_2 , is $\sim \frac{5}{N} \left| \frac{\rho \text{cm}^3}{\text{g}} \right| \left(\frac{\text{kW}}{\text{cm}^2} \right)$ (where ρ is the cathode density), which is an appreciable number.

The above idealized argument is intended to suggest that there are some interesting properties associated with micro ionic devices characterized by high power densities and short time constants. Very important factors have been ignored in the above estimate. The kinetic hindrance effects at the cathode-anode interface have been entirely neglected. The actual mechanism of the intercalation has been modeled by a single neutral entity diffusion coefficient, \tilde{D} . With regard to the latter, one piece of experimental evidence

suggests that diffusion constants can be increased even higher if the film dimension i.e. the c-axis dimension (\perp to the conducting planes) is decreased. Scholz et al. (Scholz et al, 1981) find for Ag intercalation into TaS_2 an increase in the velocity of the stage I intercalation rate by a factor of 5 for thicknesses along the c-axis of less than 500Å. These experiments in liquid electrolytes if they can be reproduced in suitable solid electrolytes, for example polymeric electrolytes, suggest another possible mode for a cathode consisting of a dispersion of micro crystals of dimension $< 500\text{Å}$ but of sufficient concentration so that the percolation threshold for the medium is exceeded. The discharge characteristics of such a disordered cathode, doubly disordered in both particulate size and particulate position have not been worked out in detail. Some preliminary calculations on a similar problem have been undertaken by West et al. (West et al, 1982) and by Nairn et al. (Nairn et al, 1983). Such a dispersed electrode problem lends itself immediately to effective medium theories for the conducting and discharge properties. Rather surprisingly such analysis do not seem to have been undertaken for this important problem.

As far as the actual mechanism of intercalation in the layered chalcogenides is concerned one can only say that the detailed mechanism is not completely understood. The static phenomena are still to a certain extent controversial. This is evident in the theories of staging in the dichalcogenides. Variations on the theory of Safran for staging in the graphite intercalation compounds (Safran and Hamann, 1981) have been applied to the transition metal dichalcogenides by Dahn et al. (Dahn et al, 1982) and Millman et al. (Millman et al, 1982). These are both phenomenological theories for the electrostatic and lattice modulated strain interactions between intercalate particles and host lattice. The dynamics of intercalation and staging has not yet been treated. The intercalate island formation and dynamics and its connection to the Hørold picture has not been clarified (Scholz, 1982) and has not been described in a microscopic calculation of the intercalation dynamics.

Kinetic effects introduced by the surface between cathode and electrolyte will be important in rates calculations for currents of the order of exchange currents. Typically, it has been difficult to characterize a pristine interface and separate effects of a mechanical nature, i.e. stresses and void formation, from the charge transfer kinetics at the interface. The situation for liquid electrolytes is better since here contact problems do not exist. The analogous situation for solid state systems is the contact between glassy and polymer electrolytes with ion insertion or intercalation compounds. Some attempts to characterize the charge transfer mechanism have been carried out for silver insertion compounds with vitreous electrolytes (Bonino et al, 1980 ; 1983 ; Patriarca et al, 1982). Beyond the phenomenology of the Butler-Volmer approach, however, the microscopic dynamics of interfacial transfer even in liquid electrolytes is controversial (Conway, 1977). The situation for the solid-solid interface is even less clear.

Here, however, it seems that the application of the small polaron model used by Beni (Beni, 1980) in the treatment of the electrochromic interface is generally applicable to transfer at a solid-solid interface, the parameters entering the theory being the interfacial transfer integral and small polaron binding energy in both phases, electrode and electrolyte. This approach as Beni has shown is capable of giving the LDK (Levich, 1970) as a special case for electron transfer. The small polaron point of view introduced by Mahan (Mahan and Pardee, 1974 ; Pardee and Mahan, 1975) while of questionable applicability for the hopping transport in typical uniform solid electrolytes may thus have an application at the electrochemical solid/solid interface. None of the details of such an approach have been worked out. Much work is needed in this area. In particular this approach should be compared with the phenomenological treatments of the frequency dependent conductivity measurements as proposed by Mac Donald et al (Mac Donald et al, 1980) which lead to equivalent circuits for interfacial capacitances.

As a general statement in summary we can remark that although theories of fast ion transport in bulk media have been developed to a reasonable degree of completeness (although much remains to be done related to the inclusion of pair interaction effects in hopping models (Dieterich et al, 1980 ; Bunde et al, 1982, 1983)), the theory of ion transport across solid-solid interfaces is still in its infancy (or even prenatal stage). There are theoretical and experimental indications that significant size effects may occur in very thin films of cathode and electrolyte materials provided that interfacial integrity is maintained. These requirements suggest that polymeric electrolytes of the polyethylene oxide class or vitreous electrolytes are the preferred components for electrolyte layers combined with ion insertion compounds for energy density and recycling considerations. Solid state cells composed of Li foil anodes, 35 μ m (PEOxLiF₃CSO₃) polymer electrolytes and 70 μ m V₆O₁₃ - carbon composite cathodes have been fabricated at AERE Harwell with cell voltages in the range 2-3 volts and current densities under cycling 0.1-1 mA/cm². (North and Hooper, 1983). These encouraging results are indicative that progress in materials research will lead to further improvement in interfacial properties and a layer technology for fast ion conducting devices.

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